

Filler-containing paper and a method for the production of filler-containing paper

Description

5 The present invention relates to filler-containing paper and to a method for the production of filler-containing paper; more particularly, it relates to filler-containing paper such as base paper for construction materials, India paper or tip base paper for cigarettes which has excellent properties such as opacity and whiteness, etc, by efficiently fixing and uniformly dispersing, in the paper, an inorganic compound comprising titanium
10 dioxide and/or calcium carbonate, and to a method for the efficient production of this filler-containing paper.

The properties demanded of paper include not only strength and degree of sizing but also optical properties such as the opacity and whiteness. In particular, taking the case
15 of paper for construction materials typified by the base paper for decorative laminated sheet, since this is affixed to a base material, opacity is demanded so that the base material region is not visible therethrough. Furthermore, in the case of the India paper used for dictionaries and the like, it is important that text and images are not visible from the reverse side. In the case of the tip base paper used in the filter region of ciga-
20 rettes, as well as it being necessary that a large amount of inorganic material be incorporated into the paper so that it does not readily catch fire in the presence of a flame, opacity is required so that the part of the filter region containing active carbon is not visible through the white tip paper which is not usually printed over its entire surface.

25 Moreover, recently, even in the case of paper for books, PPC (plain paper copier) paper and ordinary printing and writing paper, known as coated paper, the problem has arisen of a lowering of the level of opacity due to the trend for paper weight to be reduced from the point of view of more economic use of pulp resources, so a method for improving the filler efficiency in the paper is required.

30 In order to enhance the optical characteristics of paper, namely the whiteness and opacity, there is known the method of performing papermaking with the addition to the pulp slurry of papermaking fillers typified by calcium carbonate and titanium dioxide. In particular, titanium dioxide has a high light scattering capacity and is widely used for
35 the purposes of conferring a high level of opacity on paper. However, when compared to other papermaking fillers, the particle diameter of titanium dioxide is low and the yield at the time of papermaking in the papermaking machine is extremely low. Since the yield is low, build-up on and contamination of the papermaking machine and other ancillary equipment occurs. Hence, the frequency of cleaning of the papermaking machine is increased and a lowering of the production efficiency is brought about. Fur-
40 thermore, waste originating in this build-up and contamination by the filler is incorporated into the paper, leading to the problem of a lowering of paper quality. This is not restricted to titanium dioxide and even when there are used fillers such as light calcium

carbonate, if it is desired to increase the proportion of filler in the paper with the objective of enhancing the opacity it is necessary to increase the amount of filler added to the pulp slurry. However, in so doing, the amount of filler which is unfixed and is discharged into the white water system is also increased and the same kind of problems are brought about as in the case of the titanium dioxide above.

In order to raise the yield of filler, there have been used hitherto yield enhancers such as polyacrylamide resins, polyamideamine-epichlorohydrin resins or polyethyleneimine resins, etc. However, the filler yield is still inadequate and if the amount of yield enhancer added is increased in order to improve the yield there is considerable coagulation of the filler, with the result that the distribution of the filler in the paper becomes non-uniform and, in spite of their being sufficient filler present in the paper, the level of opacity of the paper remains low.

While a method is already known for enhancing filler yield by means of a polyvinylamine polymer obtained by polymerization of N-vinylformamide followed by hydrolysis of the formyl groups, in the Specification relating thereto only clay is specifically exemplified as a filler and there are no examples relating to titanium dioxide or to calcium carbonate (see JP-A-58-23809). Furthermore, in another known reference which expressly describes the titanium dioxide yield enhancing effect of a polyvinylamine polymer obtained by polymerization of N-vinylformamide followed by hydrolysis of the formyl groups, as well as the amount of added polymer being high it states that it is necessary to use an organic solvent in the polymer production process, which is undesirable for operational and environmental reasons (see JP-A-2-6685).

Furthermore, recently there have been disclosures of a method using an amphoteric water-soluble copolymer and anionic colloidal silica and/or bentonite (see Japanese Patent No.3218557) and, in particular, as a method aimed at enhancing the yield of titanium dioxide, a method of papermaking in which there are added to the pulp slurry a wet paper strengthener, sodium aluminate and alum (see JP-A-8-246389) and a method of papermaking in which carboxymethyl cellulose and aluminium sulphate are added to the pulp slurry (see JP-A-2003-89994) but, as yet, it has not been possible to achieve high opacity efficiently with just a small amount of filler.

The present invention has been made in view of this situation and has the objective of providing a filler-containing paper where, by efficiently fixing the filler to the pulp fibre without excessive coagulation thereof compared to hitherto, the ash content of the paper and the opacity of the paper are enhanced and it is possible to confer outstanding optical properties. Furthermore, the present invention also has the objective of providing a method for the production of filler-containing paper which enables the amount of filler employed at the time of papermaking to be lowered, the contamination of the papermaking machine and ancillary equipment originating in unfixed filler to be reduced,

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and a lowering of the environmental burden and an improvement in the economic efficiency to be realized.

5 The present inventors have carried out considerable investigation to resolve the aforesaid problems, as a result of which they have discovered that by carrying out paper-making with a slurry which includes (A) the hydrolysate of polymer containing at least N-vinylformamide as a polymerization component and (B) titanium dioxide and/or calcium carbonate, it is possible to obtain paper which resolves the aforesaid problems. The present invention has been perfected based on this discovery.

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Specifically, a first means for overcoming the aforesaid problems according to the present invention is

15 (1) filler-containing paper which is characterized in that it contains the following component (A) and the following component (B) and, furthermore, the ash content of the paper is 3-40 wt%.

(A) Polymer obtained by 20 to 100% hydrolysis of the total formyl groups in a polymer having at least N-vinylformamide as a polymerization component

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(B) Titanium dioxide and/or calcium carbonate

A second means for overcoming the aforesaid problems according to the present invention is

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(2)ⁱ filler-containing paper according to (1) above which is characterized in that component (A) is polymer obtained by polymerization in an aqueous medium.

A third means for overcoming the aforesaid problems according to the present invention is

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(3) filler-containing paper according to (1) or (2) which is characterized in that it is base paper for construction materials, India paper or tip base paper for cigarettes.

35 A fourth means for overcoming the aforesaid problems according to the present invention is

(4)ⁱⁱ a method for the production of filler-containing paper which is characterized in that component (A) described in (1) or (2) above is added to the pulp slurry such that the percentage addition of said component (A) to the pulp slurry is least 0.0005% but less than 0.05% by solids concentration conversion in terms of the pulp.

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A fifth means for overcoming the aforesaid problems is

- (5) a method for the production of filler-containing paper according to (4) which is characterized in that component (A) and component (B) described in (1) or (2) above are added to the pulp slurry such that the mass ratio of said component (A) to component (B) described in (1) or (2) is of proportions [component (A)/component (B)] = 0.001/100 to 0.5/100 by solids concentration conversion.

In accordance with the present invention, it is possible to enhance the ash content of the paper and the level of paper opacity, and to confer outstanding optical properties on the paper, by efficiently fixing the filler to the pulp fibre without excessive coagulation thereof when compared to hitherto. Moreover, the amount of filler used at the time of production can be reduced, the contamination of the papermaking machine and ancillary equipment due to unfixed filler can be lowered, and it is possible to achieve a reduction in the environmental burden and improved economic efficiency, so the contribution of the invention to developments in the industrial field of papermaking is considerable.

The present invention is now explained in detail.

The filler-containing paper of the present invention contains component (A), which is a specified polymer, and component (B), which is a specified inorganic compound.

Component (A) in the present invention is a polymer formed by 20 to 100% hydrolysis of the total formyl groups in a polymer having at least N-vinylformamide as a polymerization component.

As examples of polymer in which at least N-vinylformamide is a polymerization component, there are the homopolymer obtained by the polymerization of N-vinylformamide and the copolymers obtained by the copolymerization of N-vinylformamide and monomers copolymerizable with N-vinylformamide (below said homopolymer and copolymer are sometimes merely referred to together as 'polymer'). In the present invention, there can also be used mixtures of homopolymer and copolymer.

Examples of the aforesaid monomers which are copolymerizable with N-vinylformamide include the following vinyl compounds with a side chain group which contains a nitrogen atom, the vinyl or propenyl esters of saturated carboxylic acids, nonionic (meth)allyl monomers, (meth)allyl monomers having a side chain which contains a cationic nitrogen atom, olefins, ethylenically-unsaturated carboxylic acids, esters or amides of these ethylenically-unsaturated carboxylic acids, monomers with a nitrile group, monomers with a sulphonic acid group, monomers with a phosphoric acid group and styrene-type monomers.

Specific examples of the aforesaid vinyl compounds with a side chain group which contains a nitrogen atom are N-vinyl carboxylic acid amides such as N-vinylacetamide and N-vinylpropionamide, N-substituted-N-vinyl carboxylic acid amides such as N-methyl-
5 N-vinylacetamide and N-ethyl-N-vinylacetamide, N-vinyl lactams such as N-vinylpyrrolidone and N-vinylcaprolactam, N-vinyl-N-alkylamines in which an alkyl group with from 1 to 6 carbon atoms is bonded to the nitrogen atom such as N-vinyl-N-methylamine and N-vinyl-N-ethylamine, and also vinyl-heterocyclic compounds such as N-vinylimidazole, 2-vinylimidazole, N-vinyl-2-methylimidazole, N-vinyl-4-methyl-
10 imidazole, N-vinyl-5-methylimidazole, N-vinyl-2-ethylimidazole, N-vinylimidazoline, N-vinyl-2-methylimidazoline, N-vinyl-2-ethylimidazoline, N-vinyloxazole and N-vinyloxazoline.

The N-vinylimidazole and N-vinylimidazoline can be employed in their free base form,
15 or they can be employed in the form obtained by neutralization with acid or in the quaternized form. Examples of said acid are mineral acids such as hydrochloric acid, carbonic acid, sulphuric acid and nitric acid, and organic acids such as sulphonic or carboxylic acids like formic acid, acetic acid and propionic acid. The quaternization can be carried out for example using an alkyl halide such as methyl chloride or methyl bro-
20 mide, an aralkyl halide such as benzyl chloride or benzyl bromide, a dialkyl sulphate such as dimethyl sulphate or diethyl sulphate, or an epihalohydrin such as epichlorohydrin or epibromohydrin.

As examples of the aforesaid vinyl esters of saturated carboxylic acids, there are vinyl
25 formate, vinyl acetate, vinyl propionate and vinyl butyrate, and as examples of the propenyl esters of saturated carboxylic acids, there are propenyl formate, propenyl acetate and propenyl propionate.

Examples of the aforesaid nonionic (meth)allyl monomers include (meth)allyl alcohols
30 such as allyl alcohol and methallyl alcohol, (meth)allyl halides such as allyl chloride, allyl bromide, methallyl chloride and methallyl bromide, (meth)allyl ethers in which an alkyl group with from 1 to 18 carbons is ether-bonded such as allyl methyl ether, allyl ethyl ether, methallyl methyl ether and methallyl ethyl ether, and (meth)allyl esters of saturated carboxylic acids with from 1 to 18 carbons such as allyl formate, allyl acetate,
35 allyl propionate, methallyl formate and methallyl acetate.

Examples of the aforesaid (meth)allyl monomers with a side chain group which contains a cationic nitrogen atom are (meth)allylamines like allylamine and methallylamine, N-alkyl (meth)allylamines which have an alkyl group with from 1 to 18 carbons bonded
40 to the nitrogen atom such as N-methylallylamine, N-ethylallylamine, N-stearylallylamine, N-methylmethallylamine and N-ethylmethallylamine, N,N-dialkyl (meth)allylamines which have alkyl groups with from 1 to 18 carbons bonded to the

nitrogen atom such as N,N-dimethylallylamine, N,N-diethylallylamine, N,N-dimethylmethallylamine, N,N-diethylmethallylamine, N-methyl-N-stearyl-methallylamine and N,N-distearylmethallylamine, N,N,N-trialkyl (meth)allylammonium halides which have alkyl groups with from 1 to 18 carbons bonded to the nitrogen atom such as

5 N,N,N-trimethylallylammonium chloride, N,N,N-triethylammonium chloride, N,N,N-trimethylmethallylammonium chloride, N,N,N-triethylmethallylammonium chloride, N-methyl-N,N-distearylmethallylammonium chloride and N,N-dimethyl-N-stearyl-methallylammonium chloride, di(meth)allylamines such as diallylamine and di-methallylamine, N-alkyl di(meth)allylamines which have an alkyl group with from 1 to 18

10 carbons bonded to the nitrogen atom such as N-methyldiallylamine, N-ethyldiallylamine, N-methyldimethallylamine, N-ethyldimethallylamine and N-stearyldimethallylamine, and N,N-dialkyl di(meth)allylammonium halides which have alkyl groups with from 1 to 18 carbons bonded to the nitrogen atom such as N,N-dimethyldiallylammonium chloride, N,N-diethyldiallylammonium chloride, N,N-

15 dimethyldimethallylammonium chloride, N,N-diethyldimethallylammonium chloride and N,N-distearyldimethallylammonium chloride.

The aforesaid (meth)allylamines, N-alkyl(meth)allylamines, N,N-dialkyl(meth)allylamines and N-alkyldi(meth)allylamines can be employed in their free

20 base form, or they can be employed in the form obtained by neutralization with acid or in the quaternized form. Examples of said acid are mineral acids such as hydrochloric acid, carbonic acid, sulphuric acid and nitric acid, and organic acids such as sulphonic or carboxylic acids like formic acid, acetic acid and propionic acid. The quaternization can be carried out for example using an alkyl halide such as methyl chloride or methyl

25 bromide, an aralkyl halide such as benzyl chloride or benzyl bromide, a dialkyl sulphate such as dimethyl sulphate or diethyl sulphate, or an epihalohydrin such as epichlorohydrin or epibromohydrin.

As examples of the aforesaid olefins, there are ethylene, propylene and butadiene.

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As examples of the aforesaid ethylenically-unsaturated carboxylic acids there are acrylic acid, methacrylic acid, crotonic acid, maleic acid, maleic anhydride, fumaric acid, itaconic acid, itaconic anhydride, citraconic acid, citraconic anhydride, cinnamic acid, vinyl ester acids, 2-(meth)acrylamidoglycolic acid, α,β -unsaturated-tricarboxylic acids

35 and α,β -unsaturated tetracarboxylic acids, together with the alkali metal salts, alkaline earth metal salts and ammonium salts thereof.

Examples of the aforesaid ethylenically unsaturated carboxylic acid esters are (meth)acrylate esters in which an alkyl group with from 1 to 18 carbon atoms is ester-bonded, such as methyl acrylate, methyl methacrylate, ethyl acrylate, ethyl methacrylate, isobutyl methacrylate, tert-butyl methacrylate, 2-ethylhexyl acrylate and stearyl acrylate, (meth)acrylate esters where only a single hydroxy group has been esterified

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such as hydroxyethyl acrylate, hydroxyethyl methacrylate, hydroxypropyl acrylate, hydroxybutyl acrylate, hydroxypropyl methacrylate, hydroxybutyl methacrylate, 2-methoxybutyl acrylate, 2-methoxybutyl methacrylate and the acrylic acid monoesters of polyalkylene glycols of molecular weight 500 to 10,000, and the esters of an aminoalcohol and (meth)acrylic acid such as dimethylaminoethyl acrylate, dimethylaminoethyl methacrylate, diethylaminoethyl acrylate, diethylaminoethyl methacrylate, dimethylaminopropyl acrylate, dimethylaminopropyl methacrylate, diethylaminopropyl acrylate, dimethylaminobutyl acrylate and diethylaminobutyl acrylate.

These carboxylic acid esters of aminoalcohols can be employed in their free base form, or they may be employed in the form obtained by neutralization with acid or in the quaternized form. Examples of said acid are mineral acids such as hydrochloric acid, carbonic acid, sulphuric acid and nitric acid, and organic acids such as sulphonic or carboxylic acids like formic acid, acetic acid and propionic acid. The quaternization can be carried out for example using an alkyl halide such as methyl chloride or methyl bromide, an aralkyl halide such as benzyl chloride or benzyl bromide, a dialkyl sulphate such as dimethyl sulphate or diethyl sulphate, or an epihalohydrin such as epichlorohydrin or epibromohydrin.

The aforesaid amides of the ethylenically-unsaturated carboxylic acids include the N-alkyl monoamides and N-alkyldiamides of monoethylenically unsaturated carboxylic acids which have an alkyl group with from 1 to 6 carbons, examples of which are acrylamide, methacrylamide, N-methylacrylamide, N,N-dimethylacrylamide, N-methylmethacrylamide, N-ethylacrylamide, N-isopropylacrylamide and N-tert-butylacrylamide, and N,N-dialkylaminoalkyl (meth)acrylamides such as dimethylaminoethyl acrylamide, dimethylaminoethyl methacrylamide, diethylaminoethyl acrylamide, diethylaminoethyl methacrylamide, dimethylaminopropyl acrylamide, diethylaminopropyl acrylamide, dimethylaminopropyl methacrylamide and diethylaminopropyl methacrylamide.

The aforesaid N,N-dialkylaminoalkyl (meth)acrylamides can be employed in their free base form, or they can be employed in the form obtained by neutralization with acid or in the quaternized form. Examples of said acid are mineral acids such as hydrochloric acid, carbonic acid, sulphuric acid and nitric acid, and organic acids such as sulphonic or carboxylic acids like formic acid, acetic acid and propionic acid. The quaternization can be carried out for example using an alkyl halide such as methyl chloride or methyl bromide, an aralkyl halide such as benzyl chloride or benzyl bromide, a dialkyl sulphate such as dimethyl sulphate or diethyl sulphate, or an epihalohydrin such as epichlorohydrin or epibromohydrin.

Examples of the aforesaid monomers with a nitrile group are acrylonitrile, methacrylonitrile and 2-methylene-glutaronitrile.

- Examples of the aforesaid monomers with a sulphonic acid group are vinylsulphonic acid, allylsulphonic acid, methallylsulphonic acid, isoprenesulphonic acid, 3-allyloxy-2-hydroxy-propanesulphonic acid, styrene-sulphonic acid, 3-sulphopropyl acrylate, 2-acrylamido-2-methylpropanesulphonic acid, 2-methacrylamido-2-methylpropanesulphonic acid, sulphoethyl acrylate, the sulphate ester of hydroxyethyl acrylate and the sulphate ester of polyoxyalkyleneoxide acrylate, together with the alkali metal salts, alkaline earth metal salts and ammonium salts, etc, of these acids.
- 10 As examples of the aforesaid monomers with a phosphoric acid group, there are vinylphosphonic acid and styrene-phosphonic acid, together with the alkali metal salts, alkaline earth metal salts and ammonium salts, etc, of these acids.
- As examples of the aforesaid styrene-type monomers, there are styrene *per se*, α -methylstyrene, α -methylstyrene dimer and vinylbenzylamine. The vinylbenzylamine can be employed in its free base form, or it can be employed in the form obtained by neutralization with acid or in the quaternized form. Examples of said acid are mineral acids such as hydrochloric acid, carbonic acid, sulphuric acid and nitric acid, and organic acids such as sulphonic or carboxylic acids like formic acid, acetic acid and propionic acid. The quaternization can be carried out using for example an alkyl halide such as methyl chloride or methyl bromide, an aralkyl halide such as benzyl chloride or benzyl bromide, a dialkyl sulphate such as dimethyl sulphate or diethyl sulphate, or an epihalohydrin such as epichlorohydrin or epibromohydrin.
- 25 Additionally it might be advantageous to modify the described copolymers by adding monomers, which contain at least 2 non-conjugated ethylenically double bonds. Suitable monomers of this type for example are:
- 30 N,N'-methylenebisacrylamide, polyethylene glycol diacrylates and polyethylene glycol dimethacrylates, which are in each case derived from polyethylene glycols of a molecular weight from 126 to 8500, preferably 400 to 2000, trimethylolpropane triacrylate, trimethylolpropane trimethacrylate, ethylene glycol diacrylate, propylene glycol diacrylate, butanediol diacrylate, hexanediol diacrylate, hexanediol dimethacrylate, diacrylates and dimethacrylates of block copolymers of ethylene oxide and propylene oxide, polyhydric alcohols di- or triesterified with acrylic acid or methacrylic acid, such as glycerol or pentaerythritol, triallylamine, tetraallylethylenediamine, divinylbenzene, diallyl phthalate, polyethylene glycol divinyl ethers of polyethylene glycols of a molecular weight from 126 to 4000, trimethylolpropane diallyl ether, butanediol divinyl ether, pentaerythritol triallyl ether and/or divinylethylenimine.
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Preferred examples are triallylamine, allylethers of multifunctional polyols and divinylethylenurea. Usually less than 5 % of these monomers are applied. Preferred are quantities between 0,0001 % and 1 %.

- 5 In the production of the aforesaid N-vinylformamide polymer, there may be used any polymerization method such as an ionic polymerization method like anionic or cationic polymerization, or a radical polymerization method. It is preferred that there be adopted a radical polymerization method (see JP-A-11-322849) from the point of view of ready control of the molecular weight.

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The production of the mentioned N-vinylformamide polymers can be carried out by solution polymerisation, emulsion polymerisation, suspension polymerisation or precipitation polymerisation. The polymerisation is generally run in an atmosphere free of oxygen. This can be achieved by feeding a current of inert gas through the reaction mixture during the polymerisation or by degassing the reaction mixture beforehand and running the polymerisation under pressure of an inert gas or under reduced pressure.

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Despite the fact that polymerisations in non-aqueous media are also known, for examples in JP-A-2-6685 or in EP-374-646, methods in aqueous media are preferred both from the point of view of the operating environment and because no recovery equipment for the non-aqueous medium is required.

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Therefore solution polymerisations are preferably run in water, where the concentration of the monomers ranges from 5 to 60 mass%. Furthermore, in the case of emulsion polymerisation, the polymerisation is preferably carried out in an oil-in water emulsified state normally using an aqueous suspension of monomer concentration 20 – 70 mass% and an emulsifier. Also preferred are aqueous dispersions of water soluble N-vinylformamide polymers as for example described in DE-A-19851024 or WO-A-2003046024.

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In producing an aforesaid copolymer of N-vinylformamide and monomer copolymerizable with said N-vinylformamide, there can be produced a graft polymer or a block polymer by graft polymerization or block copolymerization of the N-vinylformamide and monomer copolymerizable with said N-vinylformamide.

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The aforesaid copolymer can be produced by the copolymerization of 90 to 1 mol% of the N-vinylformamide and 10 to 99 mol% of the monomer copolymerizable therewith, preferably 95 to 50 mol% and 5 to 50 mol% respectively.

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In the production of the aforesaid polymer, it is possible to use a normal polymerization initiator as the radical polymerization catalyst employed in the polymerization reaction, in particular in a radical polymerization reaction. As the polymerization initiator, there

- can be used for example an azo type polymerization initiator, a persulphate, a peroxide, a bromate, a perborate, a percarbonate or a perphosphate. Specifically, as the azo type polymerization initiator, there can be used azobisisobutyronitrile, 2,2'-azobis-(2,4'-dimethylvaleronitrile), 2,2'-azobis(4-methoxy-2,4-dimethylvaleronitrile), 2,2'-azobis(2-methylpropionitrile), 2,2'-azobis(2-methylbutyronitrile), 1,1'-azobis-(cyclohexane-1-carbonitrile), 2,2'-azobis-[2-methyl-N-(2-hydroxyethyl)propionamide], dimethyl 2,2'-azobis(2-methylpropionate), 2,2'-azobis-(2-amidinopropane), 2,2'-azobis-(2-amidinopropane), 2,2'-azobis-(N,N'-dimethyleneisobutylamine), 2,2'-azobis-(N,N'-dimethyleneisobutylamine), 2,2'-azobis(2-(2-imidazolin-2-yl)propane), 2,2'-azobis(2-(2-imidazolin-2-yl)propane) or 4,4'-azo-bis-(4-cyanovaleric acid) and the salts thereof. As examples of the persulphate, there are sodium persulphate, potassium persulphate and ammonium persulphate. As examples of the peroxide, there are benzoyl peroxide, hydrogen peroxide, tert-butylhydroperoxide and di-tert-butylperoxide. As examples of the bromate, there are sodium bromate and potassium bromate. As examples of the perborate, there are sodium perborate and ammonium perborate. As examples of the percarbonate, there are sodium percarbonate, potassium percarbonate and ammonium percarbonate. As examples of the perphosphate, there are sodium perphosphate, potassium perphosphate and ammonium perphosphate.
- These polymerization initiators can be used on their own or they can be used in combinations of two or more. Especially preferred initiators are 2,2'-azobis-4-amidinopropane hydrochloride or acetate, the sodium salt of 4,4'-azobis-4-cyanovaleric acid, and azobis-N,N'-dimethyleneisobutylamidine hydrochloride or sulphate.
- Furthermore, by jointly employing a reducing agent such as a sulphite like sodium sulphite, a bisulphite like sodium bisulphite, a metabisulphite like sodium metabisulphite, an organic amine like N,N,N',N'-tetramethylethylenediamine, or a reducing sugar like an aldose, the peroxide type polymerization initiators can also be used in the form of redox type polymerization initiators. These reducing agents can be used on their own or in combinations of two or more.

Polymerization is initiated by the addition of the polymerization initiator to the monomer solution. Moreover, with the objective of reducing the amount of unreacted monomer, a supplementary addition of some polymerization initiator may be made during the course of the polymerization reaction, or continuous addition of the polymerization initiator may be performed by a means such as the dropwise addition method. It is also possible to use the method of irradiating with ionizing radiation, an electron beam or ultraviolet light. These methods may be employed on their own or there can be used a combination of two or more types.

At the time of the polymerization, where required a chain transfer agent can be suitably employed. Examples of the chain transfer agent are compounds having one or more

hydroxy groups in the molecule, compounds having one or more mercapto groups in the molecule, compounds having one or more carbon-carbon unsaturated bonds in the molecule, peroxides such as dibutylperoxide, and hypophosphoric acid. The chain transfer agents may be used on their own or in combinations of two or more.

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Furthermore, at the time of polymerization, a crosslinking agent may be suitably added where required. Examples of the crosslinking agent are bifunctional polymerizable vinyl monomers such as di(meth)acrylates, bis(meth)acrylamides and divinyl esters which possess two unsaturated bonds, monomers with a crosslinking action due to having functional groups which undergo chain transfer with vinyl groups, monomers which have a crosslinking action due to having groups which react with vinyl groups, trifunctional polymerizable vinyl monomers which have three unsaturated bonds, tetra-functional polymerizable vinyl monomers which have four unsaturated bonds, water-soluble aziridinyl compounds, water-soluble polyfunctional epoxy compounds and silicon based compounds. These can be used on their own or in combinations of two or more.

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Furthermore, insofar as the objectives of the present invention are not impaired, the polymerization of the N-vinylformamide or the copolymerization of the N-vinylformamide and monomer copolymerizable therewith can be carried out in the presence of a water-soluble polymer such as a starch like oxidized starch, cationic starch, amphoteric starch or enzyme-modified starch, a cellulose derivative such as carboxymethylcellulose, polyvinyl alcohol, chitosan or a gum, etc.

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The component (A) in the present invention is obtained by hydrolysis of the formyl groups in polymer in which at least N-vinylformamide is a polymerization component. The hydrolysis can be carried out using a known hydrolysis method such as for example an acidic hydrolysis method, a basic hydrolysis method, a method of acidic hydrolysis in a hydrophilic solvent such as alcohol containing water, or an alcoholysis method under acidic conditions, either in the solution state or after dehydrating or drying to produce a powder state. Amongst these methods of hydrolysis, the acidic and basic hydrolysis methods are preferred.

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The modifying agent used in acidic hydrolysis can be any compound which acts as a strong acid such as hydrochloric acid, hydrobromic acid, hydrofluoric acid, sulphuric acid, nitric acid, phosphoric acid, sulfamic acid or methanesulphonic acid, but a monobasic acid is preferred in terms of facilitating the dissolution of the hydrolysate in water.

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The modifying agent used in basic hydrolysis may be any compound which acts as a strong base such as sodium hydroxide, potassium hydroxide, lithium hydroxide or a quaternary ammonium hydroxide.

As examples of the alcohol used in the case of alcoholysis, there are alcohols with from 1 to 4 carbons such as methanol, ethanol, isopropanol and butanol, but methanol is preferred.

- 5 The amount of modifying agent used for the hydrolysis will be suitably selected in accordance with the desired percentage modification, normally from within the range 0.2 to 5 times the molar quantity of the formyl groups in the aforesaid polymer, so that the percentage hydrolysis of the formyl groups in the polymer is 20-100 mol%. The reaction temperature at the time of the hydrolysis is normally in the range 30 to 110°C, and
10 the reaction time is normally from 0.1 to 24 hours.

- The percentage hydrolysis of the formyl groups in the polymer in which at least N-vinylformamide is a polymerization component is from 20% to 100% and preferably 50 to 100% of the total formyl groups in the polymer. If the percentage hydrolysis is too
15 low, there is insufficient filler fixing effect and paper opacity enhancement effect.

- When carrying out the hydrolysis, for the purposes of preventing the gelling brought about by impurities, the modification may be conducted with the optional addition of a gelling inhibitor such as hydroxylamine hydrochloride or hydroxylamine sulphate. Furthermore, hydrolysis can also be carried out after performing treatment with the gelling
20 inhibitor prior to modification. The hydrolysis can be conducted in a homogeneous solution using water or a mixture of water and a polar solvent such as methanol, or in a heterogeneous solution comprising a non-polar solvent such as hexane or toluene and a polar solvent containing at least water.

- 25 By means of the aforesaid polymerization process or process of derivative preparation, the solids concentration of the solution of polymer in which at least N-vinylformamide is a polymerization component and/or of derivative thereof obtained is normally from 3 to 40 mass%. Furthermore, when the viscosity of this polymer solution and/or derivative
30 solution is measured with a Brookfield rotary viscometer at 25°C, normally it is no more than 100,000 mPa.s and preferably no more than 20,000 mPas. In the present invention, this solution of polymer and/or of derivative can be employed as it is for use as the fixing agent.

- 35 Component (B) in the present invention is titanium dioxide and/or calcium carbonate. Put another way, component (B) in the present invention is at least one type of inorganic compound selected from the group comprising titanium dioxide, light calcium carbonate and heavy calcium carbonate. The ash content of the filler-containing paper in the present invention lies in the range 3 to 40 wt% and, along with aforesaid component (B), it is possible to use the inorganic compounds normally used as fillers for paper
40 such as kaolin, talc, clay, white carbon, aluminium hydroxide and the like. Fur-

thermore, there is no objection to incorporating filler derived from waste paper, providing it is within the aforesaid range.

5 The titanium dioxide used in the present invention may either be of the anatase or rutile type. Furthermore, there can also be used material which has been coated with alumina or silica. Normally, in the case where titanium dioxide is added to a papermaking system, it is usually employed in a slurry state dispersed in water and, in such circumstances, in order that the titanium dioxide be uniformly dispersed there may be used a dispersing agent such as sodium polyacrylate. However, there does not have to be
10 used a dispersing agent and there may also be employed in the present invention material which does not use a dispersing agent.

The calcium carbonate used in the present invention may be light calcium carbonate or heavy calcium carbonate. As light calcium carbonate, there can be used the material
15 obtained by a method such as reacting carbon dioxide with milk of lime, and as heavy calcium carbonate there can be used the material obtained by grinding crystalline limestone or marble. Normally, in the case where calcium carbonate is added to a papermaking system, it is usually used in a slurry state dispersed in water and, in such circumstances, in order to uniformly disperse the particular type of calcium carbonate
20 there may be used a dispersing agent such as sodium polyacrylate. However, there does not have to be used a dispersing agent and there may also be employed in the present invention material which does not use a dispersing agent.

There are no particular restrictions on the pulp employed as the paper raw material in
25 the present invention but it is preferred that it be a pulp used in the production of paper for construction materials, India paper or tip base paper for cigarettes. For example, there can be used kraft pulp, sulphite pulp and other such bleached and unbleached chemical pulps, groundwood pulp, mechanical pulp, thermomechanical pulp, chemithermomechanical pulp and other such bleached or unbleached high-yield pulps,
30 and also pulps containing pulp from waste paper such as newspaper, magazine paper, cardboard and the like. As well as wood pulp, there may also be used non wood-based pulps such as those based on straw or kenaf. Furthermore, there may be used a mixture of an aforesaid pulp and a synthetic fibre such as polyamide, polyester, polyolefin or polyvinyl alcohol, etc.

35 Component (A) and component (B) can be added to the pulp slurry prior to the dryer part of the papermaking process, and the method of addition is not particularly restricted, but it is preferred that they be added to the pulp slurry prior to the wet web formation. There are no particular restrictions on the order of addition of component
40 (A) and component (B) to the pulp slurry, and both may be added to the pulp slurry at the same location or they may be mixed together just before their addition to the pulp slurry. Furthermore, one may be added to the pulp slurry prior to the other.

In the case where component (A) and component (B) are added to the pulp slurry prior to the wet web formation, they may be added at the same time as, or before or after, other chemical agents. There are no particular restrictions on these chemical agents, examples of which include coagulants, dry paper strengtheners, wet paper strengtheners, sizing agents, fillers other than component (B), yield enhancers and drainage enhancers, and these are added where required so that there may be manifested the properties required in accordance with the paper type, or so that the operational characteristics are enhanced. One such chemical agent may be incorporated or there may be used two or more types in combination.

Examples of the aforesaid coagulants are poly(diallyldimethylammonium chloride) and the reaction product of amines and epihalohydrins. Examples of the dry paper strengtheners are anionic polyacrylamide, cationic polyacrylamide, amphoteric polyacrylamide, cationic starch and amphoteric starch. Examples of the wet paper strengtheners are polyamide epichlorohydrin resins, polyamine epichlorohydrin resins, melamine formaldehyde resin and urea formaldehyde resin, etc.

Furthermore, examples of the sizing agents are fatty acid soaps, solution rosin, acidic rosin emulsion, neutral rosin emulsion, alkenylsuccinic anhydride emulsion or its hydrolylate salts, 2-oxetanone emulsion, paraffin wax emulsion, cationic sizes obtained by the reaction of a carboxylic acid and a polyfunctional amine, emulsions of the reaction products of aliphatic oxyacids and aliphatic amines or aliphatic alcohols, and cationic styrene type sizes.

Examples of yield enhancers are anionic high molecular weight polyacrylamides, cationic high molecular weight polyacrylamides, amphoteric high molecular weight polyacrylamides, silica sol and bentonite, etc.

Examples of drainage enhancers are polyethyleneimine, anionic polyacrylamide, cationic polyacrylamide and amphoteric polyacrylamide, while examples of other types of chemical agent include alum, polyaluminium chloride and other types of aluminium compounds, dyes, defoaming agents and pH regulators.

The levels of addition of component (A) and component (B) to the pulp slurry should be adjusted such that the ash content in the paper lies in the range 3 to 40 wt%.

The percentage addition of component (A) to the pulp slurry is normally at least 0.0005% but less than 0.05%, preferably at least 0.001% and no more than 0.04% in terms of the dry mass of raw material pulp. If the amount of component (A) added is less than 0.0005%, then there may be an inadequate filler yield enhancement effect and an inadequate effect in raising the opacity. Conversely, if the amount of compo-

nent (A) added is 0.05% or more then, while the filler yield enhancement effect is excellent, there is considerable coagulation of the pulp fibre and filler, and there may be a reduction in the properties of the paper such as a deterioration in texture and inadequate improvement in the opacity.

5

The level of addition of component (B) is not particularly restricted but should be such that the ash content of the paper is from 3 to 40 wt%. Normally, the amount added to the pulp slurry is from 3 to 100 wt%. With regard to the percentage addition of component (B), in actual papermaking part of all of the starting material may comprise component (B) from waste paper or damaged paper, and since it is necessary to adjust the ash content according to changes in the filler contained in such starting material, the amount of component (B) added may also vary.

10

The weight ratio of component (A) to component (B), by conversion to solids concentration, preferably lies in the range [component (A)/component (B)] = 0.001/100 to 0.5/100, and more preferably [component (A)/component (B)] = 0.01/100 to 0.3/100. If the weight ratio of [component (A)/component (B)] is less than 0.001, there may be an insufficient filler yield enhancement effect and an inadequate effect in raising the opacity. Conversely, if the weight ratio of [component (A)/component (B)] is more than 0.5 then, while the filler yield enhancement effect is excellent, there is considerable coagulation of the pulp fibre and filler, and there may be a reduction in the properties of the paper such as a deterioration in texture and inadequate improvement in the opacity.

15

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Examples

Below, the present invention is explained in further detail by providing examples and comparative examples. As examples of paper production, the following three sets of conditions are exemplified but the present invention is not to be restricted in any way by these examples. Unless otherwise stated, reference to “%” means mass percent.

Paper production example 1 paper containing titanium dioxide, under acidic conditions

Paper production example 2 paper containing titanium dioxide, under neutral conditions

Paper production example 3 paper containing calcium carbonate, under neutral conditions

15

Component (A) Production Example 1

80 g (1125 mmol) of N-vinylformamide was dissolved in 385 g of water in a 2L capacity flask equipped with a stirrer, thermometer and means for operating under a nitrogen atmosphere. 0.65 g (2.4 mmol) of 2,2'-azobis-(2-amidinopropane) hydrochloride was mixed therewith and, by introducing nitrogen, oxygen was eliminated. The reaction mixture was then heated to 55°C within 1 hour. After maintaining for 5 hours at this temperature, in order to enhance the conversion the temperature was then raised to 60°C for 30 minutes and the percentage conversion made 100%. Next, 114.5 g (1129.4 mmol) of 36% aqueous hydrochloric acid solution was mixed with the viscous polymer solution thus obtained, and heating carried out for 2 hours at 90°C so that hydrolysis was performed. In the aqueous polymer solution I of cationic resin obtained, the solids concentration of the polymer was 8.6%. The viscosity of the aqueous polymer solution was 1100 mPas (Brookfield viscosity, 25°C) and it was confirmed by ¹H-NMR that 95% of the formyl groups were hydrolysed.

30

Component (A) Production Example 2

Reaction was carried out in the same way as in Example 1 except that instead of the 114.5 g (1129.4 mmol) of 36% aqueous hydrochloric acid solution used in Component (A) Production Example 1, there was mixed 68.5 g (676 mmol) of 36% aqueous hydrochloric acid solution. There was obtained aqueous polymer solution II of cationic resin, where the polymer solids concentration in the aqueous polymer solution was 12.0%, the viscosity was 1400 mPas (Brookfield viscosity, 25°C) and 60% of the formyl groups were hydrolysed (confirmed by ¹H-NMR).

40

Component (A) Production Example 3

Reaction was carried out in the same way as in Component (A) Production Example 1 except that instead of the 114.5 g (1129.4 mmol) of 36% aqueous hydrochloric acid solution used in Component (A) Production Example 1, there was mixed 34.25 g (338 mmol) of 36% aqueous hydrochloric acid solution. There was obtained aqueous polymer solution III of cationic resin, where the polymer solids concentration in the aqueous polymer solution was 14.1%, the viscosity was 2400 mPas (Brookfield viscosity, 25°C) and 30% of the formyl groups were hydrolysed (confirmed by ¹H-NMR).

Example 1 (Paper Production Example 1)

Based on the solids concentration mass ratio in terms of the absolute dry mass of pulp, 1.5% alum, 1.0% of a commercial cationic starch and 0.3% of a rosin emulsion type size (commercial name "AL1208", produced by the Seiko PMC Corporation) were added in turn to a 2.4% pulp slurry (LBKP/NBKP = 9/1, Canadian Standard Freeness 400). After stirring, the pulp slurry was diluted with pure water to 0.5% and then 20% of anatase type titanium dioxide and 0.012% (by conversion to polymer solids concentration) of the aqueous polymer solution I of cationic resin obtained in Component (A) Synthesis Example 1 were added to the pulp slurry, followed by 0.01% of cationic polyacrylamide type polymeric yield enhancer. Some of this pulp slurry was taken and a test of the fixing of component (B) carried out.

The fixing test was carried out using equipment identical to the Modified Dynamic Drainage Tester described on page 171 of TAPPI Papermakers Conference (1985) [of construction whereby the pulp slurry is poured into a jar of diameter 7.5 cm, stirred at a rotation rate of 600 rpm and air conveyed from the bottom in such a way that no mat is formed and, at the same time as the stirring and air-conveyance are halted, filtering is performed]. 500 ml of pulp slurry was filtered with a 100 mesh strainer and 100 ml of filtrate collected, then the light transmittance (%) at 620 nm measured. The higher the value of this light transmittance, the clearer the filtrate, indicating that fine fibre and filler were not discharged into the filtrate but were fixed to the fibre. In particular, in the present invention, where component (B) with a high light scattering capacity was used, the light transmission was taken as being an index of the amount of component (B) contained in the filtrate.

Then, using the remaining pulp slurry, wet paper of weight per unit area 40 g/m² was obtained by means of a Noble and Wood handsheet machine. The papermaking pH at this time was 4.5. The wet paper obtained was pressed and then dried for 80 seconds at 100°C with a drum dryer. The handsheet paper obtained was conditioned for 24 hours at 23°C and 50%RH, after which measurements were made of the weight per

unit area (basis weight), the ash content of the paper and the opacity. The results are shown in Table 1.

5 The weight per unit area (basis weight) was measured in accordance with JIS P8124 "Method of Measuring the Basis Weight of Paper and Board"; the ash content of the paper was measured in accordance with JIS P8251 "Method of Measuring the Ash Content of Paper, Board and Pulp"; and the opacity was measured in accordance with JIS P8149 "Paper and Board - Opacity Test Method (paper backing) - Diffuse Illumination Method). The measurements in the examples and comparative examples de-
10 scribed below were also carried out in the same way.

Examples 2 and 3

15 Papermaking was carried out in the same way as in Example 1, except that aqueous polymer solution I was changed to the cationic resin and amount thereof shown in Table 1. The results of the measurements performed on the paper obtained in each case are also shown in Table 1.

Example 4

20 Papermaking was carried out in the same way as in Example 2, except that the position of addition of the titanium dioxide was changed to prior to the alum. The results of the measurements performed on the paper obtained are also shown in Table 1.

25 Example 5

Papermaking was carried out in the same way as in Example 4, except that the aqueous polymer solution I of cationic resin was changed to that shown in Table 1. The results of the measurements performed on the paper obtained are also shown in Table
30 1.

Comparative Example 1

35 Papermaking was carried out in the same way as in Example 1, except that no aqueous polymer solution I was added. The results of the measurements performed on the paper obtained are shown in Table 1.

Comparative Example 2

40 Papermaking was carried out in the same way as in Example 4, except that no polymer solution I was added. The results of the measurements performed on the paper obtained are shown in Table 1.

Comparative Examples 3 and 4

5 Papermaking was carried out in the same way as in Example 1, except that polyethyleneimine was added instead of aqueous polymer solution I in the amounts shown in Table 1. The results of the measurements performed on the paper obtained are also shown in Table 1.

Comparative Example 5

10 Papermaking was carried out in the same way as in Example 1, except that instead of adding aqueous polymer solution I the amount of added cationic polyacrylamide type polymeric yield enhancer was as shown in Table 1. The results of the measurements performed on the paper obtained are also shown in Table 1.

Comparative Example 6

20 Papermaking was carried out in the same way as in Example 4, except that instead of aqueous polymer solution I there was added the amount shown in Table 1 of polyethyleneimine. The results of the measurements performed on the paper obtained are also shown in Table 1.

Table 1

| | Cationic Resin | Amount Added (%) | Ash Content of Paper (%) | Opacity (%) | Light Transmission of Filtrate in Test of Fixing (%) |
|------------|-----------------------------|-------------------------|---------------------------------|--------------------|---|
| Example 1 | aqueous polymer solution I | 0.012 | 8.5 | 81.5 | 29.7 |
| Example 2 | aqueous polymer solution I | 0.024 | 8.7 | 81.6 | 33.8 |
| Example 3 | aqueous polymer solution II | 0.024 | 8.4 | 82.0 | 29.0 |
| Example 4 | aqueous polymer solution I | 0.024 | 9.0 | 82.2 | 29.8 |
| Example 5 | aqueous polymer solution II | 0.024 | 8.8 | 82.0 | 29.5 |
| Comp.Ex. 1 | - | - | 7.5 | 80.9 | 18.4 |
| Comp.Ex. 2 | - | - | 7.6 | 79.6 | 14.9 |
| Comp.Ex. 3 | PEI | 0.0125 | 7.5 | 80.3 | 18.9 |
| Comp.Ex. 4 | PEI | 0.025 | 7.2 | 79.8 | 19.8 |
| Comp.Ex. 5 | polymeric yield enhancer | 0.01 | 8.2 | 81.2 | 19.1 |
| Comp.Ex. 6 | PEI | 0.05 | 8.2 | 80.9 | 20.6 |

PEI = polyethyleneimine

- 5 polymeric yield enhancer = cationic polyacrylamide type polymeric yield enhancer

It is clear from the results shown in Table 1 that, by means of the titanium dioxide yield enhancing effect of the present invention, there is obtained a more outstanding titanium dioxide fixing effect than in the case of the conventionally-employed polyethyleneimine (Comparative Examples 3, 4 and 6) or in the case where the added amount of cationic polyacrylamide type polymeric yield enhancer was increased (Comparative Example 5). In other words, by means of the present invention the build-up of unfixed titanium dioxide within the papermaking system is reduced and contamination of the papermaking machine and ancillary equipment is suppressed.

15 Example 6 (Paper Production Example 2)

Based on the solids concentration mass ratio in terms of the absolute dry mass of pulp, 2% of polyamidepolyamine-epichlorohydrin resin (commercial name "WS4020", produced by the Seiko PMC Corporation), 0.024% (by conversion to polymer solids concentration) of the aqueous polymer solution I of cationic resin obtained in Component

(A) Synthesis Example 1, 100% rutile type titanium dioxide, 1% alum and 0.9% sodium aluminate were added in turn to a 2.4% pulp slurry (LBKP/NBKP = 9/1, Canadian Standard Freeness 440). After stirring, the pulp slurry was diluted with pure water to 0.5%. Papermaking was carried out using this pulp slurry by means of a Noble and Wood handsheet machine, and wet paper of weight per unit area 80 g/m² obtained. The papermaking pH at this time was 7.2. The wet paper was pressed and then dried for 80 seconds at 100°C with a drum dryer. The handsheet paper obtained was conditioned for 24 hours at 23°C and 50%RH, after which measurements were made of the weight per unit area, the ash content of the paper and the opacity. The results are shown in Table 2.

Example 7

Table 2 shows the results of measurements in the case of handsheet paper obtained in the same way as in Example 6 except that the added amount of aqueous polymer solution I was as shown in Table 2.

Example 8

The same procedure was followed as in Example 6, except that the position of addition of the aqueous polymer solution I was changed to after the dilution of the pulp slurry with pure water to 0.5%.

Examples 9 and 10

Table 2 shows the results of measurements in the case of handsheet paper obtained in the same way as in Example 8 except that aqueous polymer solution I was changed to the cationic resin and amount thereof shown in Table 2.

Comparative Example 7

Table 2 shows the results of measurements in the case of handsheet paper obtained in the same way as in Example 6 except that there was no addition of aqueous polymer solution I.

Comparative Example 8

Table 2 shows the results of measurements in the case of handsheet paper obtained in the same way as in Example 7 except that instead of aqueous polymer solution I there was added polyamidepolyamine-epichlorohydrin resin.

Table 2

| | Cationic Resin | Amount Added (%) | Ash Content of Paper (%) | Opacity (%) |
|------------|-----------------------------|-------------------------|---------------------------------|--------------------|
| Example 6 | aqueous polymer solution I | 0.024 | 29.7 | 96.5 |
| Example 7 | aqueous polymer solution I | 0.036 | 30.6 | 96.7 |
| Example 8 | aqueous polymer solution I | 0.024 | 31.8 | 96.6 |
| Example 9 | aqueous polymer solution I | 0.036 | 32.7 | 96.7 |
| Example 10 | aqueous polymer solution II | 0.024 | 32.1 | 96.7 |
| Comp.Ex.7 | - | - | 27.4 | 95.7 |
| Comp.Ex.8 | PAE | 0.036 | 27.6 | 95.8 |

PAE = polyamidepolyamine-epichlorohydrin resin

- 5 From the results in Table 2, it is clear that by means of the titanium dioxide yield enhancing effect of the present invention there can be obtained paper with a higher ash content and opacity than in the case of using the conventionally-employed polyamide-polyamine-epichlorohydrin resin (Comparative Example 8), and this is suitable for the decorative laminate base paper which falls into the category of construction material
- 10 base paper.

Example 11 (Paper Production Example 3)

- Based on the solids concentration mass ratio in terms of the absolute dry mass of pulp,
- 15 0.5% of commercial cationic starch, 0.3% of AKD size (commercial name "AD1602", produced by the Seiko PMC Corporation) and 35% light calcium carbonate were added in turn to a 2.4% pulp slurry (LBKP/NBKP = 9/1, Canadian Standard Freeness 250). After stirring, the pulp slurry was diluted with pure water to 0.5% and 0.0006% (by conversion to polymer solids concentration) of aqueous polymer solution I of cationic resin
- 20 obtained in Component (A) Synthesis Example 1 added to the pulp slurry. Papermaking was carried out using this pulp slurry by means of a Noble and Wood handsheet machine, and wet paper of weight per unit area 35 g/m² obtained. The papermaking pH at this time was 8.0. The wet paper was pressed and then dried for 80 seconds at

100°C with a drum dryer. The handsheet paper obtained was conditioned for 24 hours at 23°C and 50%RH, after which measurements were made of the weight per unit area, the ash content of the paper and the opacity. The results are shown in Table 3.

5 Examples 12-17

Table 3 shows the results of measurements in the case of handsheet paper obtained in the same way as in Example 11 except that the aqueous polymer solution I was changed to the cationic resin and the amount thereof shown in Table 3.

10

Comparative Example 9

Table 3 shows the results of measurements in the case of handsheet paper obtained in the same way as in Example 11 except that there was no addition of aqueous polymer solution I.

15

Comparative Examples 10 and 11

Table 3 shows the results of measurements in the case of handsheet paper obtained in the same way as in Example 11 except that instead of aqueous polymer solution I there was added the amount shown in Table 3 of polyethyleneimine (PEI).

20

Table 3

| | Cationic Resin | Amount Added (%) | Ash Content of Paper (%) | Opacity (%) |
|------------|------------------------------|-------------------------|---------------------------------|--------------------|
| Example 11 | aqueous polymer solution I | 0.0006 | 15.6 | 87.6 |
| Example 12 | aqueous polymer solution I | 0.0012 | 16.1 | 86.1 |
| Example 13 | aqueous polymer solution I | 0.0024 | 17.3 | 87.8 |
| Example 14 | aqueous polymer solution II | 0.0012 | 15.6 | 88.8 |
| Example 15 | aqueous polymer solution II | 0.0024 | 16.9 | 89.6 |
| Example 16 | aqueous polymer solution III | 0.0012 | 15.8 | 88.4 |
| Example 17 | aqueous polymer solution III | 0.0024 | 16.6 | 87.7 |
| Comp.Ex.9 | - | - | 14.7 | 84.2 |
| Comp.Ex.10 | PEI | 0.0013 | 14.5 | 85.5 |
| Comp.Ex.11 | PEI | 0.0025 | 15.1 | 85.5 |

PEI = polyethyleneimine

- 5 From the results in Table 3 it is clear that by means of the calcium carbonate yield enhancing effect of the present invention it is possible to obtain a higher ash content and opacity that in the case of increasing the added amount of conventionally-used polyethyleneimine (Comparative Examples 10 and 11) and, as well as cigarette tip base paper and India paper, this can be applied to ordinary paper for books, PPC, coated
- 10 base paper and the like.